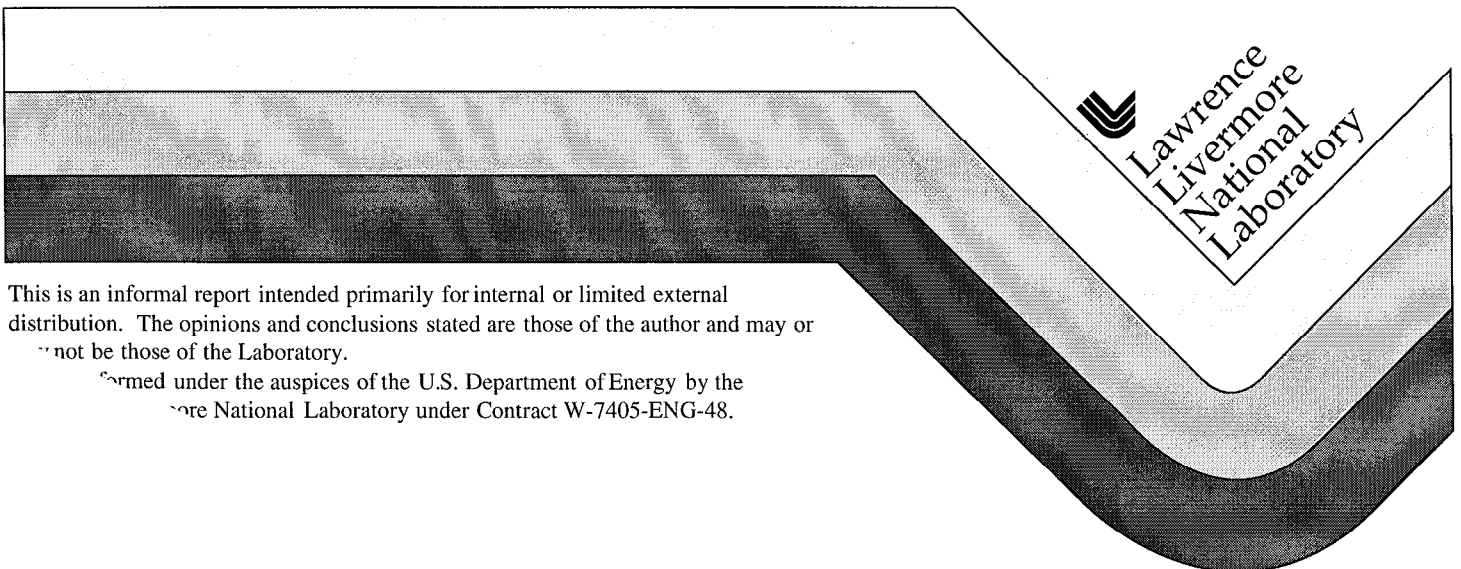


# **Activity Plan for Activity E-20-81: Development & Experimental Validation of Crevice Corrosion Models**

J. C. Farmer

December 28, 1998



 Lawrence  
Livermore  
National  
Laboratory

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Formed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

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## **Activity Plan for Activity E-20-81**

### **Development & Experimental Validation of Crevice Corrosion Models**

#### **1.0 Scientific Investigation Plan**

This Activity Plan (AP) is written for the specific activity known as “Development & Experimental Validation of Crevice Corrosion Models” (E-20-81). However, this AP may also be relevant and applicable to several other activities. These include: “Critical Crevice Potential Measurements” (E-20-44); “Geometric Aspects of Crevice Corrosion” (E-20-48); “Advanced Technique Development in Microelectrodes: (E-20-70); “Advanced Technique Development in Microanalytical Systems” (E-20-71); “Advanced Technique Development in Passive Film Property Measurements” (E-20-72); “Other Localized Corrosion Model Development” (E-20-82); and “Development of Corrosion Damage Functions” (E-20-88). These activities are listed in the “Scientific Investigation Plan for Metal Barrier Selection and Testing” (SIP-CM-01, Rev. 3, WBS #1.2.2.5.1, Section 2.5). This work is to be accomplished in accordance with Quality Assurance Requirements Document (QARD) requirements as implemented by the Lawrence Livermore National Laboratory (LLNL) Yucca Mountain Project (YMP) Quality Procedures (QP’s). Relevant QP’s include “Assurance” (033-YMP-QP 2.0); “Preparation, Approval and Revision of Procedures, Requirements and Plans” (033-YMP-QP 2.1); and “Scientific Investigation Control” (033-YMP-QP 3.0). Any Technical Implementing Procedures (TIP’s); Individual Software Plans (ISP’s); or Scientific Notebooks (SN’s) necessary for this activity will be prepared in accordance with the YMP QP entitled “Scientific Investigation and Control” (033-YMP-QP 3.0).

#### **1.1 Activity Identity**

Activity E-20-81, referred to here as Development & Experimental Validation of Crevice Corrosion Models, is an important component of a larger activity known as Modeling of Performance Behavior. Modeling of Performance Behavior is in turn a part of the Scientific Investigation Plan (SIP) for Metal Barrier Selection and Testing (SIP-CM-01, Rev. 3, WBS #1.2.2.5.1). This activity regards the integrated development and experimental validation of a general crevice corrosion model for the Engineered Barrier System (EBS). It is recognized that experiments will be required for developing and validating the crevice corrosion model. Experimental work will also be required to quantify the values of any parameters that must be fit to experimental data.

## **1.2 Responsibilities**

Key personnel responsible for performing the work in this activity are:

Technical Area Leader (TAL) Engineered Barrier Systems (EBS)	Willis Clarke
Deputy Technical Area Leader Engineered Barrier Systems	Daniel McCright
Principle Investigator (PI), Engineered Barrier Systems	Joseph Farmer
Laboratory Manager Engineered Barrier Systems	John Estill

## **2.0 Scope, Purpose & Objectives**

Alloy 22 [UNS N06022] is now being considered for construction of high level waste containers to be emplaced at the potential repository at Yucca Mountain or elsewhere. In essence, this alloy is 21% Cr, 13% Mo, 4% Fe, 3% W, 2% Co, with the balance being Ni. Variants without tungsten are also being considered. Detailed mechanistic models are being developed to account for the corrosion of Alloy 22 surfaces in crevices that will inevitably form. Such occluded areas experience substantial decreases in pH, with corresponding elevations in chloride concentration. Other relevant materials will also be investigated: nickel-based alloys such as Alloys 825, 625, C-4, C-276 and 59; titanium-based alloys such as Grades 12, 7 and 16, carbon steels such as A516 Grade 55; stainless steels such as 304, 304L, 316, 316L and 316NG; various copper-based alloys; and any materials that would serve as crevice formers (rock, thermally-sprayed ceramics, etc.). Experimental work has been undertaken to validate the crevice corrosion model, including parallel studies with 304 stainless steel. The crevice corrosion model is described in detail in scientific notebooks of the Principal Investigator, as well as other publications. Codes will be prepared in accordance with the YMP QP entitled "Software Quality Assurance" (033-YMP-QP 12.0).

Initially, the high-level waste containers will be hot and dry due to the heat generated by radioactive decay. However, the temperature will eventually drop to levels where both humid air and aqueous phase corrosion will be possible. Crevices will be formed between waste package and supports; beneath mineral precipitates, corrosion products, dust, rocks, cement and biofilms, and between double-wall containers. It is well known that the crevice environment will be more severe than the NFE. The hydrolysis of dissolved metal will lead to the accumulation of  $H^+$  and the corresponding suppression of pH. Field-driven electromigration of  $Cl^-$  (and other anions) into the crevice must occur to balance cationic charge associated with  $H^+$  ions [9.1 through 9.3]. The exacerbated conditions inside the crevice set the stage for subsequent attack of the CRM by passive corrosion, pitting (initiation & propagation), stress corrosion cracking (initiation &

propagation), or other mechanisms. Clearly, the development of an adequate crevice corrosion model for determination of the exact nature of the local environment is prudent.

Alloy 22 has several desirable attributes that make it an attractive candidate for fabrication of high-level waste containers. It is less susceptible to localized corrosion (LC) than Alloys 825 and 625, that were leading candidates in earlier designs [9.4]. The unusual LC resistance of Alloy 22 is believed to be due to the additions of both Mo and W, which should stabilize the passive film at very low pH [9.5]. Elemental analyses of surface films should be done with X-ray photoelectron spectroscopy (XPS). In regard to the addition of tungsten to Alloy 22, note that  $\text{WO}_3$  appears to be less soluble at low pH than  $\text{MoO}_2$  and  $\text{MoO}_3$ . This material therefore exhibits a very high repassivation potential, approaching that required for  $\text{O}_2$  evolution [9.6]. The repassivation potential is believed to be the threshold for initiation of LC. In experiments with simulated crevice solutions (10 wt. %  $\text{FeCl}_3$ ), very low (passive) corrosion rates are observed [9.7 through 9.8]. Finally, no significant localized attack of Alloy 22 was observed in crevices exposed to simulated acidified water (SAW) for one year. These tests were conducted in the Long Term Corrosion Test Facility (LTCTF) at Lawrence Livermore National Laboratory (LLNL) [9.9]. However, we have observed the crevice corrosion of Alloy 22 during anodic polarization at very high potentials (1.2 V vs. SCE) and ambient temperature in electrolytes saturated with chloride salts.

A variety of research is being conducted at LLNL, directed towards possible degradation modes of Alloy 22. Corrosion modeling for Total System Performance Assessment (TSPA) is a key component of this work. Models include simple correlations of experimental data [9.9], as well as detailed mechanistic models necessary for believable long-term predictions [9.4 through 9.5]. These models are fully described in scientific notebooks of the Principal Investigator, as well as in other related publications. Several interactive modes of corrosion are possible and have made it necessary to develop a wide variety of models that should ultimately be integrated. These process-level models include those to account for the inhibition of corrosion by protective ceramic coatings, pH suppression and  $\text{Cl}^-$  elevation in crevices, pit initiation and propagation, as well as stress corrosion and hydrogen-induced cracking. This activity plan addresses the development and experimental validation of process-level models to account for corrosion of Alloy 22 and other relevant surfaces exposed directly to the exacerbated conditions in crevices.

Crevice formed with Alloy 22 and other materials of construction will lead to a localized environment with suppressed pH and elevated chloride, even in cases where the passive film remains stable. However, the electrochemical potential inside the crevice is expected to be well below that at the mouth, which will probably be well below the repassivation potential. Therefore, catastrophic localized breakdown of the passive film inside the crevice is not expected. This is consistent with atomic force microscopy (AFM) of surfaces inside such crevices [9.5]. These conditions are expected to lead to an enhancement of the passive corrosion rate inside the crevice. It is predicted that the corrosion product remaining on the Alloy 22 surface is enriched in tungsten. The role of Mo and W in the passivation of this alloy should be investigated in detail with XPS. In

cases where one of the barriers is made of a titanium-based alloy, work must also be done to assure that no cathodic hydrogen charging occurs in the acidic crevice environment. In some cases, hydrogen absorption might lead to hydrogen-induced cracking.

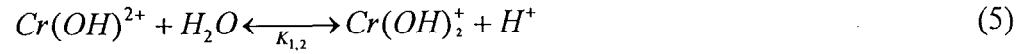
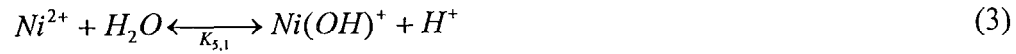
### 3.0 Activity Description

#### 3.1 Modeling Approach

*Summary.* A detailed deterministic model is to be further developed to calculate the spatial distributions of electrochemical potential and current density in crevices, as well as transient concentration profiles of dissolved metals and ions [9.4 through 9.5]. Note that all equations given here are discussed in detail in Reference 9.4, as well as in the scientific notebooks of the Principal Investigator. It is assumed that the local concentration of hydrogen ions is limited by either (a) anion transport or (b) the rate of hydrolysis. If the limitation is assumed to be due to anion transport, all hydrolysis reactions at each point inside the crevice are assumed to instantaneously reach equilibrium. Furthermore, it is assumed that electroneutrality is maintained at each point. In contrast, if the limitation is assumed to be hydrogen ion production and transport, the local generation rate of hydrogen ion must be known and is assumed to be proportional to the dissolution rates of dissolved metals, with proportionality constants being calculable from hydrolysis equilibrium constants. Any data not generated under the Quality Assurance Requirements Document (QARD), such as hydrolysis equilibrium constants, will have to be accepted in accordance with "Acceptance of Data Not Generated Under the Control of the QARD" (033-YMP-QP 2.5). Note that rate constants for the hydrolysis reactions are unknown, with experimental determination being impractical. In this case, anion concentrations are calculated at each point based upon electroneutrality. This model can be used to estimate the extent of pH suppression in crevices due to the simultaneous hydrolysis and transport of dissolved Fe, Ni, Cr, Mo and W. At the present time, dissolved metal species included in the calculation are  $\text{Fe}^{2+}$ ,  $\text{Fe}(\text{OH})^+$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}(\text{OH})^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ni}(\text{OH})^+$ ,  $\text{Cr}^{3+}$ ,  $\text{Cr}(\text{OH})^{2+}$ ,  $\text{Cr}(\text{OH})_2^+$ ,  $\text{Mo}^{3+}$  and  $\text{WO}_4^{2-}$ . Possible precipitates include  $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{Ni}(\text{OH})_2$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{MoO}_2$  and  $\text{WO}_3$ . The solubilities of various oxides and hydroxides believed to be formed during dissolution of Alloy 22 are given by Pourbaix [9.10]. As previously stated, any data not generated under the QARD will have to be accepted in accordance with the YMP QP entitled "Acceptance of Data Not Generated Under the QARD" (033-YMP-QP 2.5).

*Crevice Chemistry.* As discussed by Oldfield and Sutton, metal ions produced by anodic dissolution of iron, nickel and chromium are assumed to undergo the following hydrolysis reactions [9.1]:





Relevant equilibrium constants are defined as follows [9.1 and 9.11]:

$$K_{3,1} = \frac{[Fe(OH)^+][H^+]}{[Fe^{2+}]} \quad (6)$$

$$K_{4,1} = \frac{[Fe(OH)^{2+}][H^+]}{[Fe^{3+}]} \quad (7)$$

$$K_{5,1} = \frac{[Ni(OH)^+][H^+]}{[Ni^{2+}]} \quad (8)$$

$$K_{1,1} = \frac{[Cr(OH)^{2+}][H^+]}{[Cr^{3+}]} \quad (9)$$

$$K_{1,2} = \frac{[Cr(OH)_2^+][H^+]}{[Cr(OH)^{2+}]} \quad (10)$$

If the dissolved metals exceed the solubility limits, precipitation will occur:



The corresponding solubility products are:

$$K_{3,3} = [Fe^{2+}][OH^-]^2 \quad (14)$$

$$K_{5,3} = [Ni^{2+}][OH^-]^2 \quad (15)$$

$$K_{1,3} = [Cr^{3+}][OH^-]^3 \quad (16)$$

It is assumed that anodic dissolution reactions are depolarized by the cathodic reduction of dissolved oxygen or hydrogen evolution [9.12]. As the model is developed, equilibria for other species involving dissolved Mo, W and Ti will have to be included. The impact of  $Cl^-$ ,  $F^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $CO_3^{2-}$ , and other anions will also have to be considered.

*Method 1: Rate of Hydrolysis Limits  $H^+$  Concentration.* Hydrolysis reactions of various dissolved metal ions will result in pH suppression within the crevice. In order to quantify this effect, it is necessary to account for the net accumulation of hydrogen ions. The corresponding mass balance is:

$$[H^+] = [H^+]_{Fe(II)} + [H^+]_{Fe(III)} + [H^+]_{Ni(II)} + [H^+]_{Cr(III)} - [H^+]_{H_2} - [H^+]_{O_2} \quad (17)$$

At the present time, the effects of hexavalent chromium, molybdenum and tungsten on pH are assumed to be insignificant during application of Method 1. The quantity of hydrogen ions generated by the hydrolysis of divalent iron ions produced during the dissolution of either the CAM or CRM is:

$$[H^+]_{Fe(II)} = 2[Fe(OH)_2](s) + [Fe(OH)^+] \quad (18)$$

The dissolved  $Fe^{2+}$  can be converted to  $Fe^{3+}$  by: (i) microbial action; (ii) oxidation by naturally occurring  $MnO_2$  or other oxidants; or (ii) anodic oxidation. Once formed, it is assumed that  $Fe^{3+}$  can also undergo hydrolysis. The quantity of hydrogen ions produced by this reaction is:

$$[H^+]_{Fe(III)} \approx [Fe(OH)^{2+}] \quad (19)$$

Dissolution of the CRM will produce divalent nickel and trivalent chromium ions, in addition to divalent iron ions. The equations for the divalent nickel are analogous to those for the divalent iron:

$$[H^+]_{Ni(II)} = 2[Ni(OH)_2](s) + [Ni(OH)^+] \quad (20)$$

The equations for the trivalent chromium are similar to those for the trivalent iron:

$$[H^+]_{Cr(III)} = 3[Cr(OH)_3](s) + 2[Cr(OH)_2^+] + [Cr(OH)^{2+}] \quad (21)$$



Hydrogen ions lost due to hydrogen evolution and the cathodic reduction of oxygen are represented by:

$$[H^+]_{H_2} = 2[H_2] \quad (22)$$

$$[H^+]_{O_2} = 4[O_2] \quad (23)$$

As previously discussed, all equations can be found in Reference 9.4 or the scientific notebooks of the Principal Investigator. Equations 18 through 23 are substituted into Equation 17. The concentrations of soluble hydrolysis products are then expressed in terms of  $[H^+]$  and the concentrations of unhydrolyzed metal ions. The result is then differentiated with respect to time to yield the following  $H^+$  generation rate:

$$\frac{d[H^+]}{dt} = \frac{\left\{ \frac{K_{3,1}}{[H^+]} \frac{d[Fe^{2+}]}{dt} + \frac{K_{4,1}}{[H^+]} \frac{d[Fe^{3+}]}{dt} + \frac{K_{5,1}}{[H^+]} \frac{d[Ni^{2+}]}{dt} + \frac{K_{1,1}}{[H^+]} \frac{d[Cr^{3+}]}{dt} + \frac{2K_{1,1}K_{1,2}}{[H^+]^2} \frac{d[Cr^{3+}]}{dt} - 2 \frac{d[H_2]}{dt} - 4 \frac{d[O_2]}{dt} \right\}}{\left\{ 1 + \frac{K_{3,1}[Fe^{2+}]}{[H^+]^2} + \frac{K_{4,1}[Fe^{3+}]}{[H^+]^2} + \frac{K_{5,1}[Ni^{2+}]}{[H^+]^2} + \frac{K_{1,1}[Cr^{3+}]}{[H^+]^2} + \frac{4K_{1,1}K_{1,2}[Cr^{3+}]}{[H^+]^3} \right\}}$$

The consumption of  $H^+$  by hydrogen evolution and cathodic oxygen reduction is accounted for. Since the  $H^+$  generation rate approaches zero as  $[H^+]$  and the concentrations of unhydrolyzed metal ions approach infinity (large values), the extent of pH suppression in the crevice is limited. If solubility limits are exceeded,  $Fe(OH)_2$ ,  $Ni(OH)_2$ ,  $Cr(OH)_3$ , and other precipitates are assumed to form. Under these conditions, the  $H^+$  generation rate is proportional to the rates of precipitation, which are directly related to the rates of dissolution. The hydrolysis equilibrium constants can be found in the literature [9.1 and 9.11].

*Method 2: Electromigration Limits  $H^+$  Concentration.* An alternative strategy can be used to estimate pH suppression in the crevice. In this case, it is assumed that acidification of the crevice solution is limited by the transport of  $Cl^-$  into the crevice, instead of being limited by  $H^+$  generation and transport out of the crevice. As discussed by Pickering and others,  $Cl^-$  will be driven into the crevice by the potential gradient [9.13 through 9.15]. After the  $Cl^-$  concentration is established, the  $H^+$  concentration can be determined with the equation for electroneutrality. The roots of the resulting polynomial in  $[H^+]$  determine the pH.

*Transient Concentrations.* Attention is now directed to transport in the crevice separating the CAM and CRM. As discussed by Newman, fluxes of ions are estimated with the Nernst-Planck equation, which governs electromigration, diffusion, and convective transport [9.16]:

$$\bar{N}_i = -z_i u_i F c_i \bar{\nabla} \Phi - D_i \bar{\nabla} c_i + \bar{v} c_i \quad (25)$$

where  $N_i$  is the flux,  $z_i$  is the charge,  $u_i$  is the mobility,  $c_i$  is the concentration and  $D_i$  is the diffusivity of the  $i$ -th ion;  $\Phi$  is the potential in the electrolyte; and  $v$  is the convective velocity of the electrolyte. The current density is then defined in terms of the flux:

$$\bar{i} = -F^2 \bar{\nabla} \Phi \sum_i z_i^2 u_i c_i - F \sum_i z_i D_i \bar{\nabla} c_i \quad (26)$$

In cases with strong supporting electrolyte, the electromigration term can be ignored. Transients in concentration can be dealt with through application of Equation 26:

$$\frac{\partial c_i}{\partial t} = -\bar{\nabla} \cdot \bar{N}_i + R_i \quad (27)$$

where  $R_i$  is the (apparent) homogeneous rate. Note that the concentration of dissolved iron is assumed to include all dissolved species, including  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}(\text{OH})^+$  and  $\text{Fe}(\text{OH})^{2+}$ . Similar assumptions are made for other dissolved metals. The hyperbolic partial differential equations (PDEs) that describe the transport of such reactive species in the crevice can be solved numerically. Both the Crank-Nicholson and the explicit methods have been used [9.17 through 9.18]. The assumed boundary conditions (BC's) imply that the concentrations are zero at the crevice mouth (NFE), and that crevices are symmetric about a mirror plane where the flux is zero. The BC's for  $\text{H}^+$  and dissolved  $\text{O}_2$  are slightly different in that non-zero concentrations are assigned at the crevice mouth.

*Current and Potential.* The PDEs that define transient concentrations in the crevice require determination of the potential gradient, as well as the (apparent) homogeneous rates. First, the axial current density along the length of the crevice,  $i_x(x)$ , is calculated by integrating the wall current density,  $i_y(x)$ :

$$i_x(x) = \frac{\int_x^L i_y(x) dx}{h(x)} \quad (28)$$

where  $L$  is the maximum crevice depth and  $h(x)$  is the separation between the two crevice walls at position  $(x)$ . The electrode potential along the length of the crevice,  $E(x)$ , can then be calculated from  $i_x(x)$ :

$$E(x) = \int_0^x \rho(x) i_x(x) dx \quad (29)$$

where  $\rho(x)$  is the resistivity of the crevice solution at position  $(x)$ . This technique is very similar to that employed in other published models [9.13 through 9.15].

To illustrate the type of results expected from this activity, specific examples are given. The illustrative calculations shown here assume: (1) 25°C; (2) 170,000 ppm NaCl; (3) 0.5882  $\mu\text{S cm}^{-1}$  per ppm NaCl; (3) a diffusion coefficient of  $1.9 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$  for all dissolved species; and (4) an initial crevice width of 0.015 cm. In the case of Type 304 stainless steel, it was assumed that: (1) the potential at the mouth of the crevice is at 0.400 V vs. SCE; (2) the corrosion potential and current density are -0.400 V vs. SCE and  $1.0 \times 10^{-7} \text{ A cm}^{-2}$ , respectively; (3) the passive region extends from -0.350 to 0.350 V vs. SCE and is characterized by a passive current density of  $5.0 \times 10^{-6} \text{ A cm}^{-2}$ ; (4) the threshold potential for breakdown of the passive film is 0.350 V vs. SCE; and (5) the current density due to localized corrosion is  $1.0 \times 10^{-3}$  at 0.400 V vs. SCE. In the case of Alloy 22, it was assumed that: (1) the potential at the mouth of the crevice is at 0.800 V vs. SCE; (2) the corrosion potential and current are -0.160 V vs. SCE and  $2.0 \times 10^{-8} \text{ A cm}^{-2}$ , respectively; (3) the passive region extends from -0.100 to 0.700 V vs. SCE and is characterized by a passive current density of  $2.0 \times 10^{-6} \text{ A cm}^{-2}$ ; (4) the threshold potential for breakdown of the passive film is 0.700 V vs. SCE; and (5) the current density due to localized corrosion is  $1.0 \times 10^{-2}$  at 0.850 V vs. SCE. Application of the model to other materials will require other assumptions.

Illustrative calculations for crevice corrosion of Type 304 stainless steel are discussed first. Since the electrochemical potential (E) was predicted to decrease with increasing crevice depth, it is expected that the potential should never be more severe (closer to the threshold for LC) than at the crevice mouth. Figure 1 shows calculated values of pH and ion concentration as a function of distance from the crevice mouth. Calculations are at 600-second intervals, with the last calculated value at 3600 seconds. Values of pH estimated by Method 1 (limited by hydrolysis) and Method 2 (limited by anion transport) are both shown. Based upon Method 2, it is concluded that the pH could be 1.5 to 2.0 in a crevice that is predominately in the passive region. This general conclusion is now supported by measurements of crevice pH, which were made during development of the experimental technique for model validation, and were found to be less than two ( $\text{pH} < 2$ ). These early tests were done with saturated KCl. As computational and experimental techniques improve, exact comparisons between predictions and measurement should be possible. Simulations at higher anodic potential involve larger current densities, larger rates, and much smaller increments in time and space.

Illustrative calculations for crevice corrosion of Alloy 22 are discussed in this paragraph and are illustrated in Figures 2 through 5. Figure 2 shows calculated values of pH and ion concentration as a function of distance from the crevice mouth. Calculations are at 600 second intervals, with the last calculated value at 3600 seconds. For contrast, values of pH estimated by Method 1 (limited by hydrolysis) and Method 2 (limited by electromigration) are both shown. Based upon Method 2, it is concluded that the pH could be 1.5 to 2.0 in a crevice that is essentially passive. This general conclusion is now supported by measurements

of pH in a passive crevice formed from Alloy 22, which was found to be less than two ( $\text{pH} < 2$ ). These early tests were done with saturated KCl. Transients in the total concentrations of dissolved Fe, Ni, Cr, Mo and W at 0, 600, 1200, 1800, 2400, 3000 and 3600 seconds are shown in Figure 3. With the exception of tungsten, these concentrations rise sharply from zero at the crevice mouth to constant values (a plateau) deep inside the crevice. Recall that the concentrations are assumed to be zero at the crevice mouth. Figure 4 shows the distributions of dissolved W, which is assumed to be  $\text{WO}_4^{2-}$ , and precipitated  $\text{WO}_3$  inside the crevice. This unusual behavior is due to the retrograde dependence of tungsten solubility on pH (less soluble in acidic environments) [9.10]. At positions in the crevice with low pH, the corrosion of Alloy 22 results in the formation of solid  $\text{WO}_3$ . Near the crevice mouth, which has a higher pH, the tungsten begins to dissolve. The penetration and oxide growth rates inside the crevice are shown in Figure 5.

To the extent possible, attempts will be made to abstract relatively complicated numerical models into simplified analytical models that capture the essence of important physiochemical effects such as the suppression of pH in crevices.

### **3.2 Experimental Approach for Model Validation**

As discussed by Sedriks [9.19], the Naval Research Laboratory (NRL) has observed  $\text{pH} < 2$  in crevices made of stainless steel [9.20]. The local crevice environment is also being determined experimentally as part of this integrated activity. Thus far, crevices have been constructed from square metallic samples, 2 inches on each side and 1/8 inch thick. The samples are masked with plastic tape, thereby forming an exposed square area, 1.7 inches on each side. The exposed area is placed underneath a clear plastic window with an access port for a miniature pH sensor in the center. A second pH sensor is located at the mouth of the crevice, in close proximity to a saturated calomel reference electrode (SCE). The use of in situ sensors to determine crevice pH has also been described by Sridhar and Dunn [9.21]. In parallel experiments, paper strips with a pH-sensitive dye (pH paper) is sandwiched between the sample and the clear plastic window and photographed with a digital electronic camera in a time-lapse mode. Spectroscopic-grade graphite counter electrodes are also placed in the electrolyte lying outside the mouth of the crevice. A potentiostat is then used to control the electrochemical at the mouth of the crevice. Temperature, potential, current, and pH is then recorded electronically during the course of the experiment. Measurements of pH inside a Type 304 stainless steel crevice are shown in Figure 6. The electrochemical potential at the mouth was maintained at 0.8 V vs. SCE. Crevice corrosion could be seen initiating near the crevice mouth and propagating towards the pH sensor, which was located about 1 inch inside the crevice mouth. After about 3 hours, the corrosion front finally reached the pH sensor and the pH immediately dropped from an initial value of about 5.7 to approximately 1.4. Simultaneously, the fixed volume of electrolyte outside of the crevice became alkaline, reaching a fluctuating level between 10 and 12. Active corrosion inside

the crevice was evident since the emerald green  $\text{NiCl}_2$  solution was easily visible. In experiments with pH papers, the propagating corrosion front was accompanied by immediate acidification. This technique is illustrated by Figure 7, which are time-lapse color photographs taken with a digital camera. After polarization of the working electrode (304 stainless steel), the indicator near the crevice mouth turned red immediately (indicative of a pH between 1 and 2), with the red color spreading across the paper towards the center of the sample. Before complete acidification in the entire crevice, the nucleation of pits beneath the pH paper was easily visible as bright red dots. Clearly, the nucleated pits were serving as local sources of acid, thereby causing localized color changes in the paper. A reference indicator outside of the crevice was photographed simultaneously to serve as a reference for the color changes observed inside the crevice. Typically, the indicator outside of the crevice would turn green ( $8 < \text{pH} < 10$ ). Similar experiments were performed with Alloy 22. In this case, the working electrode (Alloy 22) remained passive at all locations inside the crevice. There was no visible evidence of localized corrosion of the metal surface underneath the clear plastic window, and no bright red dots appeared underneath the indicator paper. The acidification of a passive crevice formed from Alloy 22 is illustrated by Figure 8. Even though the crevice remained passive, the passive current density and imposed electric field within the crevice was sufficient to cause significant acidification. Here too the pH dropped relatively low levels ( $1 < \text{pH} < 2$ ). The experimental work to be conducted in accordance with this activity plan will facilitate further development of predictive models.

### **3.2.1 Procurement and Tracking of Samples**

All samples for quality effecting work will be procured and tracked as per the YMP QP's entitled "Control of Purchased Items and Services" (033-YMP-QP 7.0) and "Identification and Control of Items, Samples, and Data" (033-YMP-QP 8.0). Such work will also conform to relevant requirements set forth in the YMP TIP entitled "Labeling, Tracking, and Shipping of Samples" (TIP-YM-3). In this case, the Laboratory Manager or an appropriate alternative will procure samples for this activity in an approved manner and make those samples available to the Lead Principal Investigator for this activity. Activities directed at developing novel experimental techniques needed by the program can use samples that have not been procured and tracked by these procedures, provided that the work is not quality effecting. In these instances, the elemental composition of the samples will be determined analytically to establish consistency with the stated identity of the alloy.

### **3.2.2 Sample Metrics**

Samples used for creation of crevices will be adequately measured before and after each experiment. The 2 in. x 2 in. x 1/8 in. samples will have one face finished with a 600-grit paper. The sample will then be cleaned

and thoroughly rinsed with deionized water. The sample will be weighed with all dimensions measured prior to masking. After masking, the exposed metal area will be fully measured. The increase in sample thickness around the perimeter due to masking will also be recorded, with at least three equally spaced measurements along each edge. The measurements will be repeated after completion of the experiment, before the masking is removed, and after the masking is removed. All of the measuring and testing equipment (MT&E) used for "quality effecting work" will be labeled as "controlled" as per the YMP QP entitled "Control of Measuring and Test Equipment" (033-YMP-QP 12.0). Activities directed at developing novel experimental techniques needed by the program can use MT&E that has not been labeled as per 033-YMP-QP 12.0, provided that the work is not "quality effecting." Note that equipment labeled as per 033-YMP-QP 12.0 may not have been procured with funds from the Nuclear Waste Fund. Such labeling does not imply ownership of the equipment by the YMP.

### **3.2.3 Construction of Electrochemical Cells**

As previously described in Section 3.2, crevices are constructed from square metallic samples, 2 inches on each side and 1/8 inch thick. The samples are masked with plastic tape, thereby forming an exposed square area, 1.7 inches on each side. The exposed area is placed underneath a clear plastic window with an access port for a miniature pH sensor in the center. A second pH sensor is located at the mouth of the crevice, in close proximity to a saturated calomel reference electrode (SCE). In parallel experiments, paper strips with a pH-sensitive dye (pH paper) is sandwiched between the clear plastic window and photographed with a digital electronic camera in a time-lapse mode. Spectroscopic-grade graphite counter electrodes are also placed in the electrolyte lying outside the mouth of the crevice. Other appropriate materials can also be used as counter electrodes. A potentiostat is then used to control the electrochemical at the mouth of the crevice. Temperature, potential, current, and pH is then recorded electronically during the course of the experiment. Any custom apparatus or experimental configurations should be documented in the SN of the Principle Investigator. The SN will be controlled in accordance with the YMP QP's entitled "Scientific Notebooks" (033-YMP-QP 3.4) and "Document Control (033-YMP-QP 6.0).

### **3.2.4 Use of Standard Reference Electrodes**

Either single- or double-junction saturated calomel or Ag/AgCl reference electrodes can be used. Each electrode compartment will be checked to make sure that it is adequately filled with the appropriate filling solution (probably an aqueous solution saturated with potassium chloride). An

ensemble of such electrodes will be co-located into a single beaker with an aqueous solution saturated with potassium chloride (KCl). The temperature of the solution should be monitored. An electrometer or other digital voltmeter with sufficiently high input impedance will be used to measure each of the reference electrodes relative to one selected as an overall reference. After proper operation is assured, one of the selected reference electrodes in the ensemble can be removed from the beaker, rinsed with deionized water, placed in the electrochemical cell where the validation experiment is to be conducted, and connected to the reference lead of the potentiostat.

Properly prepared reference electrodes (half-cells) are thermodynamically-based standards and should only require documentation of the composition of the filling solution and metal used for fabrication of the electrode. For example, the Ag/AgCl electrode is prepared from high-purity silver wire. The composition of the wire used for fabricating and electrode can be determined practically by relying on supplier labels and specifications, or by performing a destructive analysis of the wire after completion of measurements. If reference electrodes are purchased and used for quality effecting work, the procurement will be done in accordance with applicable QP's. Specifically, such items will be procured from a qualified supplier in accordance with the YMP QP entitled "Control of Purchased Items and Services" (033-YMP-QP 7.0). In this case, the composition of the wire will be determined from supplier specifications. If existing reference electrodes are used for quality effecting work, the composition of the filling solution and metallic electrode can be verified by chemical analysis. Analytical verification can be done after the experimental measurements are completed since analysis of the metallic component will be destructive to the electrode. For non-quality effecting work, such as the development of novel techniques crucial to the Program, it is assumed that printed labels on reference electrodes are adequate to guarantee the identity of electrode materials. For example, a commercial reference electrode labeled as Ag/AgCl would be assumed to be made with Ag wire. Filling solutions can also be procured from a qualified supplier, or prepared from reagent grade chemicals that were procured from a qualified supplier. It must be noted that a poorly prepared reference electrode procured by QP's may provide inaccurate results. The performance of each electrode should be checked against an array of similar electrodes. Some reasonable variation between electrodes is usually observed, and is expected. All calibrations should be documented in the SN of the Principle Investigator. The SN will be controlled in accordance with the YMP QP's entitled "Scientific Notebooks" (033-YMP-QP 3.4) and "Document Control (033-YMP-QP 6.0). If desired, all observed values can be placed on a common potential scale, that of the standard hydrogen electrode (SHE). Correlations have been obtained for the electrochemical potentials of the AgCl and SCE reference

electrodes as functions of temperature. The first correlation for Ag/AgCl/0.1M KCl was provided by David Shoesmith and was developed by AECL [9.22].

$$E_{AgCl}(SHE) = 0.23755 - 5.3783 \times 10^{-4} T(^{\circ}C) - 2.3728 \times 10^{-6} T(^{\circ}C)^2 + 2.2671 \times 10^{-4} [T(^{\circ}C) + 273] \quad (30)$$

The second correlation for Hg/Hg<sub>2</sub>Cl<sub>2</sub>/satd. KCl was obtained from the well-known text by Bard & Faulkner [9.23].

$$E_{SCE}(SHE) = 0.2412 - 6.61 \times 10^{-4} [T(^{\circ}C) - 25] - 1.75 \times 10^{-6} [T(^{\circ}C) - 25]^2 - 9.0 \times 10^{-10} [T(^{\circ}C) - 25]^3 \quad (31)$$

Relevant temperature corrections can be calculated with each of these expressions, as given in Table 1 below:

Table 1. Correction of Reference Electrodes at Various Temperatures.

T (°C)	E <sub>Ag/AgCl/0.1M KCl</sub> (V vs. SHE)	E <sub>SCE</sub> (V vs. SHE)
25	0.2902	0.2412
60	0.2722	0.2344
90	0.2629	0.1906
95	0.2485	0.1861

These tabulated corrections are additive. In the case of the Ag/AgCl/0.1M KCl electrode, the potential must also be corrected for electrolyte concentration, so that it is applicable for the standard AgCl electrode with saturated KCl. First, the solubility of KCl as a function of temperature is obtained from the CRC Handbook [9.24].

$$T = 20^{\circ}C : C_{\text{saturated KCl}} = 23.8 \text{ grams per } 100 \text{ cc}$$

$$T = 100^{\circ}C : C_{\text{saturated KCl}} = 56.7 \text{ grams per } 100 \text{ cc}$$

The saturation concentrations at other temperatures is estimated by simple linear interpolation, as shown in Table 2:

Table 2. Saturation Concentration of KCl by Linear Interpolation.

T (°C)	C <sub>saturated KCl</sub> (g per 100 cc)	C <sub>saturated KCl</sub> (mol/kg)
20	23.8	3.192
25	25.86	3.468
60	40.25	5.398
90	52.59	7.053
95	54.64	7.329
100	56.7	7.605



Note that a formula weight of KCl is assumed to be approximately 74.56, and ignores any hydration effects. Activity coefficients are not included here. The Debye-Huckel equation could be used to estimate the activity coefficients, however, it only applies rigorously to infinitely dilute solutions. Other activity coefficient models for higher electrolyte concentrations are controversial, due to a general lack of knowledge of the sphere of hydration surrounding individual ions, a general inability to account for Coulombic and dipole interactions between each pair of individual ions, and other equally important effects. A simplification of the Nernst equation, which also ignores activity coefficients, can be used to make a first order correction of the potential of the Ag/AgCl/KCl reference electrode for KCl concentration. The Nernst equation can be written as:

$$E = E^0 + \frac{RT}{nF} \ln \frac{C_o}{C_R} \quad (32)$$

where the convention is assumed to be:



Application of this simplified Nernst equation to the Ag/AgCl/KCl reference electrode yields:

$$E_{Ag/AgCl/satd. KCl} - E_{Ag/AgCl/0.1M KCl} = -\frac{RT}{F} \ln \frac{C_{satd. KCl}}{C_{0.1M KCl}} \quad (34)$$

where the assumed reaction is:



Given Faraday's constant of  $9.64846 \times 10^4$  C/equiv, the value of  $RT/F$  at 25°C is 0.02569 V, and can be scaled to different temperatures (Table 3). These corrections can be applied to applied potentials, as well as measured corrosion, pitting and repassivation potentials.

Table 3. Correction of Ag/AgCl Reference Electrode for Concentration.

T (°C)	RT/F (V)	$E_{Ag/AgCl/0.1M KCl}$ (V vs. SHE)	$C_{saturated KCl}$ (mol/kg)	Concentration Correction (V)	$E_{Ag/AgCl/satd. KCl}$ (V vs. SHE)	$E_{SCE}$ (V vs. SHE)
25	0.02569	0.2902	3.468	-0.0911	0.1991	0.2412
60	0.02871	0.2722	5.398	-0.1145	0.1577	0.2344
90	0.03129	0.2629	7.053	-0.1332	0.1297	0.1906
95	0.03172	0.2485	7.329	-0.1362	0.1123	0.1861

### 3.2.5 Use and Calibration of Potentiostats

The use and calibration of potentiostats will be done in a manner which is consistent with the YMP QP entitled "Control of Measuring and Test Equipment" (033-YMP-QP 12.0). A variety of potentiostats from Princeton Applied Research (PAR) are appropriate for the experimental validation studies described here. These include Models 173, 176 and 276. Models 173 and 176 potentiostats are primarily operated in the manual mode. The Model 276 potentiostat can be operated in either manual or remote mode. In the remote mode, data acquisition is done with an IBM-compatible personal computer via a GPIB interface. Data is stored in ASCII files. In the manual mode, data is acquired via analog-to-digital converters installed in an IBM-compatible personal computer, or recorded with appropriate strip chart recorders. Other types of potentiostats and data recorders may also be appropriate. Electronic data will be controlled in accordance with the YMP QP entitled "Control of the Electronic Management of Data" (033-YMP-QP 3.8).

Potentiostats are essentially operational amplifiers. In the common adder potentiostat, the circuit forces sufficient current to flow from the counter electrode (CE) to the working electrode (WE), which is maintained at ground potential, to assure that the desired potential difference is maintained between the reference (REF) and working electrode (WE). The working electrode (WE) and ground (GND) leads from the potentiostat are connected to one end of the NIST-traceable resistor, while the counter electrode (CE) and reference electrode (REF) are connected to the opposite end. Proper calibration requires a NIST-traceable resistor (calibration standard) and a calibrated instrument for the measurement of either current or voltage. The potentiostat is programmed and activated, thereby applying a predetermined potential across the NIST-traceable resistor. For example, application of 1 volt across a one-ohm ( $1\ \Omega$ ) NIST-traceable resistor should produce a current flow of 1 amp through the resistor. The applied voltage can be verified with a calibrated instrument for voltage measurement. Alternatively, the current flowing through the resistor during application of the applied voltage can be verified with a calibrated instrument for current measurement. The applied voltage and current are related through Ohm's law (Table 4).

Table 4. Expected Results for Application of Potential Across Resistor

Potential (WE vs. REF or CE)	Current (A)
$0.00001 \pm \text{error}$	$0.00001 \pm \text{error}$
$0.0001 \pm \text{error}$	$0.0001 \pm \text{error}$
$0.001 \pm \text{error}$	$0.001 \pm \text{error}$
$0.01 \pm \text{error}$	$0.01 \pm \text{error}$
$0.1 \pm \text{error}$	$0.1 \pm \text{error}$
$1.0 \pm \text{error}$	$1.0 \pm \text{error}$

All calibrations should be documented in the SN of the Principle Investigator. The SN will be controlled in accordance with the YMP QP's entitled "Scientific Notebooks" (033-YMP-QP 3.4) and "Document Control (033-YMP-QP 6.0).

### **3.2.6 Use and Calibration of Strip Chart Recorders**

Strip chart recorders will be calibrated at the beginning of each experiment by adjusting and marking recording pen deflections with known potential inputs. The potential input can be from a calibrated standard voltage source, or from the potentiostats described in 3.2.5. All calibrations should be documented in the SN of the Principle Investigator. The SN will be controlled in accordance with the YMP QP's entitled "Scientific Notebooks" (033-YMP-QP 3.4) and "Document Control (033-YMP-QP 6.0).

### **3.2.7 Use and Calibration of Digital Data Acquisition Systems**

The digital data acquisition system can be based upon analog-to-digital convertor boards manufactured by National Instruments and compatible with a personal computer of choice. The hardware can be controlled with any appropriate software, such as National Instruments LabView or another suitable program. Digital data acquisitions systems will be calibrated at the beginning of each experiment by adjusting (with software or hardware) to match known potential inputs. The potential input can be from a calibrated standard voltage source, or from the potentiostats described in 3.2.5. All calibrations should be documented in the SN of the Principle Investigator. The SN will be controlled in accordance with the YMP QP's entitled "Scientific Notebooks" (033-YMP-QP 3.4) and "Document Control (033-YMP-QP 6.0). All data recorded by the digital data acquisition system should be controlled in accordance with the YMP QP entitled "Control of the Electronic Management of Data" (033-YMP-QP 3.8).

### **3.2.8 Use and Calibration of pH Electrodes and Monitoring Electronics**

If pH electrodes are purchased and used for quality effecting work, the procurement will be done in accordance with applicable QP's. Specifically, such items will be procured from a qualified supplier in accordance with the YMP QP entitled "Control of Purchased Items and Services" (033-YMP-QP 7.0). In this case, the composition of the pH electrode will be determined from supplier specifications. If existing pH electrodes are used for quality effecting work, the composition of the filling solution, the glass membrane, and the metallic electrode can be verified by chemical analysis. Analytical verification can be done after

the experimental measurements are completed since analysis of the metallic component will be destructive to the electrode. For non-quality effecting work, such as the development of novel techniques crucial to the Program, it is assumed that printed labels on pH electrodes are adequate to guarantee the composition of the filling solution, the glass membrane, and the metallic electrodes. Filling solutions can also be procured from a qualified supplier, or prepared from reagent grade chemicals that were procured from a qualified supplier. It must be noted that a pH electrode procured in accordance with valid QP's may provide very inaccurate results if poorly prepared. The performance of each pH electrode should be checked against an array of similar pH electrodes. Some reasonable variation between electrodes is usually observed, and is expected.

A pH sensor (glass-membrane type) with its reference electrode is connected to an appropriate electronic monitor. While such sensors come in a variety of sizes, miniaturized devices are preferred for use in this activity. All such pH electrodes will be calibrated with at least three commercially available buffer solutions. Recommended levels include pH levels of 4 (pink), 7 (green) and 10 (blue). Each sensor is rinsed in deionized water before submersion in any calibration buffer. The temperatures of the buffer solutions are measured with a thermometer or thermocouple and noted. The temperature compensation on the monitoring electronics is adjusted accordingly. A given pH sensor is first submersed in the green buffer (pH 7), given sufficient time for equilibration, and the "zero" adjusted on the electronic monitor so that the digital reading is 7.00 or better. The sensor is then removed from the green buffer, rinsed with deionized water, placed into the pink buffer (pH 4), and given sufficient time for equilibration. Then, the "slope" is adjusted so that the digital reading is 4.00 or better. Some drift is to be expected. Then, the calibrated sensor and monitoring electrode is checked again at pH levels of 7, 10 and 4. If necessary, additional adjustments are made to assure proper calibration. Several pH electrodes will be calibrated simultaneously and used as cross references for the detection of unreliable sensors. All calibrations should be documented in the SN of the Principle Investigator. The SN will be controlled in accordance with the YMP QP's entitled "Scientific Notebooks" (033-YMP-QP 3.4) and "Document Control (033-YMP-QP 6.0).

As an alternative to glass-membrane electrodes, a miniaturized pH sensor based upon laser-induced fluorescence from an excited ratiometric fluorescence dye can be used. The pH-dependent fluorescence can be sensed by with a spectrometer and a charge coupled device (CCD) array detector. This sensor is fabricated by first stripping the shield and cladding from a length of the fiber optic. Then a solution of hydrofluoric acid is used to etch the end of the fiber in such a way to form a conical end. A sol gel solution is then used to deposit a porous coating on the

conical end of the fiber. This porous sol gel coating serves as a host for an immobilized ratiometric fluorescent dye. Florescence in the tip of the fiber can be excited with the 488 nm line of an argon-ion laser. Optical filters are used to prevent the exciting wavelength, as well as other strong lines of the argon laser, from reaching the CCD array detector. Care must be taken to block the very strong 514.5 nm line.

### **3.2.9 Use and Calibration of Other Ion Specific Electrodes**

If other ion specific electrodes are purchased and used for quality effecting work, the procurement will be done in accordance with applicable QP's. Specifically, such items will be procured from a qualified supplier in accordance with the YMP QP entitled "Control of Purchased Items and Services" (033-YMP-QP 7.0). In this case, the functionality of the ion specific electrode will be determined from supplier specifications. Such ion specific electrodes are calibrated with the same general strategy discussed in Section 3.2.8, where calibration solutions for the ions of interest are substituted for the buffer solutions. All calibrations should be documented in the SN of the Principle Investigator. The SN will be controlled in accordance with the YMP QP's entitled "Scientific Notebooks" (033-YMP-QP 3.4) and "Document Control (033-YMP-QP 6.0).

### **3.2.10 Use and Calibration of Ionic Conductivity Probes**

If ionic conductivity probes are purchased and used for quality effecting work, the procurement will be done in accordance with applicable QP's. Specifically, such items will be procured from a qualified supplier in accordance with the YMP QP entitled "Control of Purchased Items and Services" (033-YMP-QP 7.0). In this case, the "cell constant" of the ionic conductivity probe will be determined from supplier specifications. Such ionic conductivity probes are calibrated with the same general strategy discussed in Section 3.2.8, where calibration solutions for the conductivities of interest are substituted for the buffer solutions. All calibrations should be documented in the SN of the Principle Investigator. The SN will be controlled in accordance with the YMP QP's entitled "Scientific Notebooks" (033-YMP-QP 3.4) and "Document Control (033-YMP-QP 6.0).

### **3.2.11 Use and Calibration of Analytical Balances**

All analytical balances shall be checked for accuracy before use by weighing a series of NIST-traceable weight standards, with the measurements of each standard weight recorded in the scientific notebook where experimental results are kept. To the extent possible, this activity will use relevant general practice described by the TIP entitled "User-

Calibration of Mettler AT200 Analytical Balances” (TIP-CM-04). However, since this TIP was prepared for a specific instrument (Mettler AT200), it may not be exactly applicable to other balances. Reasonable departures from this TIP are permissible, with the overall calibration being adequately documented in the SN of the Principle Investigator. The SN will be controlled in accordance with the YMP QP’s entitled “Scientific Notebooks” (033-YMP-QP 3.4) and “Document Control (033-YMP-QP 6.0).

### **3.2.12 Use and Calibration of Calipers**

All calipers shall be checked for accuracy before use by weighing a series of NIST-traceable dimensional standards, with the measurements of each standard weight recorded in the scientific notebook where experimental results are kept. To the extent possible, the this activity will use relevant general practice described by the YMP TIP entitled “User-Calibration of Fowler Ultra-Cal Mark III Digital Caliper, Technical Implementing Procedure” (TIP-CM-05). However, since different non-electronic calipers may be involved, it will not be followed exactly. All calibrations should be documented in the SN of the Principle Investigator. The SN will be controlled in accordance with the YMP QP’s entitled “Scientific Notebooks” (033-YMP-QP 3.4) and “Document Control (033-YMP-QP 6.0).

### **3.2.13 Use and Calibration of Thermocouples and Thermometers**

Standard Type K thermocouples are recommended for this activity. If thermometers, thermocouples and thermocouple readers are purchased for use in quality effecting work, the procurement will be done in accordance with applicable QP’s. Specifically, such items will be procured from a qualified supplier in accordance with the YMP QP entitled “Control of Purchased Items and Services” (033-YMP-QP 7.0). In this case, the composition (or type) of the thermocouple will be determined from supplier specifications. Measurements should be verified by comparison against well-known physical properties, such as the boiling point of water, or by comparison to another calibrated thermocouple and thermocouple reader of known pedigree. With proper verification and calibration, it is possible to use existing thermometers, thermocouples and thermocouple readers. Specifically, the composition of existing thermocouples can be verified by chemical analysis of the two lead wires. Appropriate chemical analysis includes X-ray fluorescence. Thermocouples and thermocouple readers should be calibrated by direct comparison to a calibrated thermocouple and thermocouple reader of known pedigree. Mercury thermometers should be checked by direct comparison to calibrated thermocouples of known pedigree. All calibrations should be documented in the SN of the Principle Investigator. The SN will be controlled in

accordance with the YMP QP's entitled "Scientific Notebooks" (033-YMP-QP 3.4) and "Document Control (033-YMP-QP 6.0).

### **3.2.14 Scientific Notebook Entries**

Scientific Notebooks (SN's) will be controlled in accordance with the YMP QP's entitled "Scientific Notebooks" (033-YMP-QP 3.4) and "Document Control (033-YMP-QP 6.0). Periodically, all pertinent data will be recorded in the scientific notebook, including the working electrode potential relative to the reference, the current flowing between the working and counter electrode, the pH in side the crevice, the pH at the crevice mouth, the solution temperature. The experimentalist will maintain full written records of the experiment to serve as a backup for electronic recording.

## **3.3 Hold Points**

The modeling and experimental validation activities will be monitored on a continuous basis by the Lead Principal Investigator to ensure that the work is proceeding according to plan. If significant unanticipated problems arise, the Lead Principal Investigator will inform the Technical Area Leader. A joint decision will be made about the future course of action.

The progress of the modeling efforts will be reported to the Technical Area Leader in periodic reports. If substantial changes in project scope require that the experimental work change significantly in direction, the Technical Area Leader will communicate this to the Lead Principal Investigator in writing. No formal hold points or decision points will be designated.

## **3.4 Equipment**

### **3.4.1 Modeling**

Numerical calculations may be performed on any suitable computer platform, IBM-compatible PC, UNIX Workstations, mainframes, or supercomputers. FORTRAN 77 (or a more recent standard) is the preferred programming language. Programs will write results in ASCII output files that are easily readable by other well-known software such as Microsoft Excel. However, any commercial graphics software may be used to present the model results. As previously discussed, macros and codes will be documented in the SN's of the Principal Investigator, and where appropriate, qualified as per the YMP QP entitled "Software Quality Assurance Plan" (033-YMP-QP 3.2). Scientific Notebooks (SN's) will be used and controlled in accordance with the YMP QP entitled "Scientific Notebooks" (033-YMP-QP 3.4).

### **3.4.2 Experimental Validation**

Experimental equipment required for model development, validation and parameter identification are specific to this activity. In the early stages of model development, necessary equipment should be identified in the Scientific Notebooks and calibration techniques should be documented there. Scientific Notebooks (SN's) will be used and controlled in accordance with the YMP QP entitled "Scientific Notebooks" (033-YMP-QP 3.4). If the work falls outside of this activity plan, a new or revised activity plan should be prepared.

### **3.5 Test Materials**

The materials involved in this activity will usually be found in the list given in SIP-CM-01 Rev. 3. However, other materials may be tested if they are judged by the PI to be useful in the modeling effort. For example, a large data base exists on the localized corrosion of austenitic stainless steels, so a limited number of experiments on such materials may be performed to validate the experimental methods being used or developed.

Test specimens will be purchased from either a YMP approved vendor, or from a vendor with a subsequent check analysis performed by a YMP approved laboratory. Documentation will be obtained from the vendor or the laboratory concerning the relevant information for each metal or alloy. In nearly all cases, the relevant information will be the ingot heat number and chemical composition of the metal/alloy, but in some cases, the thermal-mechanical processing history and resulting mechanical properties may also be of interest. The PI will make the determination of what information is needed from the vendor or laboratory and indicate this and the justification for this information in the SN. The PI will keep the test specimen documentation either in the SN or, if there are many analyses, in a SN or electronic database, referenced to and by the SN.

Generally, the values and permitted ranges of chemical composition and mechanical properties of a metal or alloy are governed by ASTM, AWS, or other appropriate metallurgical industrial standards. If the information supplied by the vendor or laboratory indicates that the composition or properties of a heat of material conform to the metallurgical industrial standards, the PI (or designee) will indicate that the material is acceptable. If the information supplied by the vendor or laboratory indicates that the composition or properties of a heat of material do not conform to the metallurgical industry standards, then the TAL (or a designee) will make a determination of the acceptance or rejection of a particular heat of material, or determine whether additional analyses are required.

If metallic samples from other sources are used for quality effecting work, the composition of the samples will be verified by chemical analysis by a YMP approved laboratory. In such cases, microstructural characterization should also



be done if adequate information on the heat cannot be obtained. Such analytical verification can be done after the experimental measurements are completed since analysis may be destructive to the sample. For non-quality effecting work, such as the development of novel techniques crucial to the Program, samples of known alloy type can be used without analytical verification.

If metallic samples are purchased and used for quality effecting work, the procurement will be done in accordance with applicable QP's. Specifically, such items will be procured from a qualified supplier in accordance with the YMP QP entitled "Control of Purchased Items and Services" (033-YMP-QP 7.0). In this case, the composition of the metallic samples be determined from supplier documentation. All analytical verification of alloy composition and microstructure should be documented in the SN of the Principle Investigator. The SN will be controlled in accordance with the YMP QP's entitled "Scientific Notebooks" (033-YMP-QP 3.4) and "Document Control (033-YMP-QP 6.0). Test materials will be handled, stored and shipped in accordance with the YMP QP entitled "Handling, Storage and Shipping" (033-YMP-QP 13.0).

### **3.6 Test Environments**

The environments used for any experimental activities will focus on the Bounding Environments identified in SIP-CM-01 Rev. 3. However, a wider range of environments may be appropriate for model development, validation, and parameter identification. Experiments may involve standard test media listed in Sections 3.6.1 through 3.6.3.

#### **3.6.1 Simulated Dilute Water (SDW)**

This medium is to be prepared in accordance with the Technical Implementing Procedure entitled "Formulation and Make-Up of Simulated Dilute Water (SDW), Low Ionic Content Aqueous Solution" (TIP-CM-06).

#### **3.6.2 Simulated Concentrated Water (SCW)**

This medium is to be prepared in accordance with the Technical Implementing Procedure entitled "Formulation and Make-Up of Simulated Concentrated Water (SCW), High Ionic Content Aqueous Solution" (TIP-CM-07).

#### **3.6.3 Simulated Acidic Concentrated Water (SAW)**

This medium is to be prepared in accordance with the Technical Implementing Procedure entitled "Formulation and Make-Up of Simulated Acidic Concentrated Water (SAW), High Ionic Content Aqueous Solution" (TIP-CM-08).

### **3.7 Technical and Readiness Reviews**

No additional formal Readiness Review (RR) is planned for this activity. No formal Technical Review (TR) is planned at the completion of the present activity. However, depending on the progress of technical work in this activity and related ones, a TR may be held to review the adequacy of the totality of physically-based modeling for making long-term performance predictions. Any formal RR will be conducted in accordance with the YMP QP entitled "Readiness Review" (033-YMP-QP 2.6). Any formal TR will be conducted in accordance with the YMP QP entitled "Technical Review" (033-YMP-QP 2.4).

The following list of materials are needed for execution of this AP:

1. Controlled scientific notebook
2. At least one NIST-traceable resistor
3. Calibrated instrument for measuring voltage or current
4. Programmable potentiostat
5. Instrumentation for electronically recording signals from instruments
6. Appropriate storage media for electronically recorded data
7. Electrochemical cell of appropriate design
8. Procured pH paper of known pedigree
9. Procured or existing reference electrodes
10. Procured or properly prepared filling solution for reference electrodes
11. Procured or existing pH electrodes and electronic meter
12. Procured or properly prepared filling solution for pH electrodes
13. Procured standard buffer solutions for calibration of pH electrodes
14. Procured or existing ion specific electrodes and electronic meter
15. Procured or properly prepared filling solution for ion specific electrodes
16. Procured standard solutions for calibration of ion specific electrodes
17. Procured or existing ionic conductivity probes and electronic meter
18. Procured standard solutions for calibration of ionic conductivity probes
19. Procured or existing thermometers, thermocouples and readers
20. Calibrated thermocouple and thermocouple reader of known pedigree
21. Procured or prepared metallic samples
22. Source of analytical services for aqueous solutions
23. Source of analytical services for metallic wires and samples

If necessary, such items will be procured from a qualified supplier in accordance with the YMP QP entitled "Control of Purchased Items and Services" (033-YMP-QP 7.0). All calibrations should be documented in the SN of the Principle Investigator. The SN will be controlled in accordance with the YMP QP's entitled "Scientific Notebooks" (033-YMP-QP 3.4) and "Document Control (033-YMP-QP 6.0).

### **3.8 Special Training & Qualification Requirements**

Qualifications of the Principal Investigator (PI) and technicians are specified by the Technical Area Leader in accordance with the YMP QP entitled "Qualification of Personnel" (033-YMP-QP-2.10). The PI shall have a Ph.D. in chemical engineering, chemistry, electrochemical engineering, electrochemistry, materials science, metallurgy, metallurgical engineering, or an equivalent scientific and technical discipline from an accredited university or institution with substantial research programs. The PI should have several (at least three) years of appropriate research experience at a research university or national laboratory following completion of the Ph.D. The PI should have experience and knowledge in numerical methods such as multivariable regression analysis, the solution of ordinary and partial differential equations, and other relevant modeling techniques. The PI should also have experience in various electrochemical measurements with potentiostats and galvanostats, AC impedance systems, reference electrodes, pH electrodes, and optical spectroscopy, as well as various methods of data acquisition. The PI should have some familiarity with the surface analytical tools necessary for ex situ characterization of samples. The PI should have published several (at least three) technical and scientific articles in relevant fields of study, such as electrochemistry, electrochemical engineering, materials science or numerical modeling. Professional awards are very desirable. Technical support staff shall have appropriate experience in electrochemical or corrosion instrumentation and techniques, with specific requirements established by the Principal Investigator. All personnel will be trained and indoctrinated in accordance with the YMP QP entitled "Indoctrination and Training" (033-YMP-QP 2.9). Only personnel trained to appropriate QP's and any other procedures of the Yucca Mountain Site Characterization Project will be allowed to participate in these activities.

### **3.9 Quality Assurance Program**

This activity will be conducted in accordance with requirements of the QARD. This activity will be monitored for compliance through surveillance. Initial development of models will be described and documented in the scientific notebooks of the Principal Investigator. Once the basic assumptions of the model have been validated and the overall approach confirmed to be sound, more detailed quality controls can be developed and implemented, which will lead to the development of a final model with appropriate experimental validation. Detailed quality controls will ultimately include readiness reviews, preparation of Individual Software Plans (ISP's), and preparation of Activity Plans (AP's). Activity Plans such as this provide a detailed discussion of the model development strategy, as well as a detailed discussion of experiments necessary to validate the model and to quantify model parameters for specific materials.

### **3.10 Activity Closeout**

As with all other activities in the "Metal Barrier Selection and Testing Task," the major reporting channel is through periodic revision of the "Engineered Materials Characterization Report" or EMCR, which is Activity E-20-39 in SIP-CM-01 Rev. 2. Supporting documentation such as SN's and technical report review comments will be retained by the appropriate individual (PI or technical support personnel) until the document package is transferred to the LLNL/YMP Local Records Center (or another authority specified by the program) at the conclusion of these activities. Many of these records are transferred periodically as record segments so that the final records package of this activity is compiled over a period of time. Quality Assurance (QA) records will be transmitted as described in the YMP QP entitled "Quality Assurance Records" (033-YMP-QP-17.0). No additional or special activity close-outs are planned.

### **4.0 Precision and Accuracy**

The precision and accuracy of numerical and experimental results depend upon the specific results being discussed. The PI should take care in reporting only significant figures in final results.

### **5.0 In-Progress Documentation**

Documentation to be generated during the conduct of these activities will include scientific notebooks, computer input and output, program listings, electronic databases, and may also include data record sheets, raw data, progress reports, and the final report. Scientific notebooks are controlled and maintained according to the YMP QP entitled "Identification and Control of Items, Samples and Data" (033-YMP-QP-8.0).

Along with other technical activities in the Metallic Barriers Task, reporting of the results of this activity will occur on a regular and periodic basis as determined by the schedule of project deliverables. Also, the results will be reported as revisions to the EMCR. As appropriate, topical LLNL reports (UCRL or UCID) will be prepared on parts of this activity. Interim reports may also be written if deemed appropriate. The report(s) will undergo technical review as specified in the YMP QP entitled "Review of Technical Publications" (033-YMP-QP-3.3).

### **6.0 Interfaces**

The collection, review and submittal of technical data will be done in accordance with the YMP QP entitled "Collection, Review and Submittal of Technical Data" (033-YMP-QP 3.6). The control of internal technical interfaces will be controlled in accordance with the YMP QP entitled "Control of Internal Technical Interfaces" (033-YMP-QP 3.5). The information obtained from these modeling activities will assist activities in the following technical areas and copies of the written reports from these activities will be distributed to the individuals designated.

**6.1 LLNL C&MS Management**

- 6.1.1 Associate Director (Hal Graboske or other)
- 6.1.2 Associate Director Staff (Jesse Yow or other)
- 6.1.3 Associate Director Staff (Bob Glass or other)
- 6.1.4 Materials Division Leader (Lloyd Chase or other)
- 6.1.5 Computational Materials Capability Leader (Bill Wolfer or other)

**6.2 CRWMS LLNL Management**

- 6.2.1 CRWMS LLNL Manager (Martha Kohler or other)
- 6.2.2 Deputy CRWMS LLNL Manager (Cynthia Palmer or other)
- 6.2.3 Engineering Assurances (Royce Monks or other)
- 6.2.4 Administrator (Barbara Bryan or other)

**6.3 Repository Advisor Committee**

- 6.3.1 Member 1 (C. K. Chou or other)
- 6.3.2 Member 2 (W. L. Clarke or other)
- 6.3.3 Member 3 (A. C. Lingenfelter or other)
- 6.3.4 Member 4 (T. G. Surles or other)
- 6.3.5 Member 5 (L. W. Younker or other)

**6.4 Metal Barrier Selection and Testing (SIP-CM-01)**

- 6.4.1 Technical Area Leader (Willis Clarke or other)
- 6.4.2 Deputy Technical Area Leader (R. Daniel McCright or other)
- 6.4.3 Principal Investigator, Corrosion Science (Greg Gdowski or other)
- 6.4.4 Principal Investigator, Surface Analytical (Peter Bedrossian or other)
- 6.4.5 Laboratory Supervisor (John Estill or other)
- 6.4.6 Secretary (Nan Poggio or other)

**6.5 Waste Form & Waste Package Internals**

- 6.5.1 Technical Area Leader (William Halsey or other)
- 6.5.2 Deputy Technical Area Leader (Steve Steward or other)
- 6.5.3 Task Leader, Spent Fuel & Cladding (Ray Stout or other)

**6.6 Licensing & Special Projects (SIP-PA-2)**

- 6.6.1 Technical Area Leader (Michael Fernandez or other)
- 6.6.2 Task Leader, Performance Assessment (William Halsey or other)
- 6.6.3 Task Leader, Near Field Environment (Nina Rosenberg or other)
- 6.6.4 Code Qualification Expert (Ed Kansa or other)

**6.7 LLNL YMP Office, Las Vegas**

- 6.7.1 Manager, LLNL YMP Office, Las Vegas (Jim Blink or other)

## 7.0 Schedule

The current PACS budget and schedule should be consulted, with any relevant changes documented in written memoranda.

## 8.0 Special Cases

No subcontractors to LLNL are involved in these activities.

## 9.0 References

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## **10.0 Appendices**

- 10.1 Figure 1. Simulated crevice corrosion of Type 304 stainless steel in saturated NaCl at 25°C with applied potential of 0.4 V vs. SCE. Predicted pH profiles at 600-second increments with lowest predicted levels at 3600 seconds.
- 10.2 Figure 2. Simulated crevice corrosion of Alloy 22 in saturated NaCl at 25°C with applied potential of 0.8 V vs. SCE. Predicted pH profiles at 600-second increments with lowest predicted levels at 3600 seconds.
- 10.3 Figure 3. Simulated crevice corrosion of Alloy 22 in saturated NaCl at 25°C with applied potential of 0.8 V vs. SCE. Predicted dissolved metal profiles at 600 second intervals with the highest values at 3600 seconds. Corresponds to Figure 2.
- 10.4 Figure 4. Simulated crevice corrosion of Alloy 22 in saturated NaCl at 25°C with applied potential of 0.8 V vs. SCE. Predicted profiles for dissolved W and precipitated WO<sub>3</sub> at 600-second intervals with the highest values at 3600 seconds. Corresponds to Figure 2.
- 10.5 Figure 5. Simulated crevice corrosion of Alloy 22 in saturated NaCl at 25°C with applied potential of 0.8 V vs. SCE. Predicted wall penetration and WO<sub>3</sub> thickness at 0.01, 0.1 and 1.0 cm from the crevice mouth. Corresponds to Figure 2.
- 10.6 Figure 6. Measured pH during crevice corrosion of 304 stainless steel in saturated KCl at 25°C with applied potential of 0.8 V vs. SCE. Measured values confirmed with indicator.
- 10.7 Figure 7. Time-lapse color photographs taken with digital camera showing changes in pH paper as the solution in a 304 stainless steel crevice becomes acidic.
- 10.8 Figure 8. Time-lapse color photographs taken with digital camera showing changes in pH paper as the solution in an Alloy 22 crevice becomes acidic.

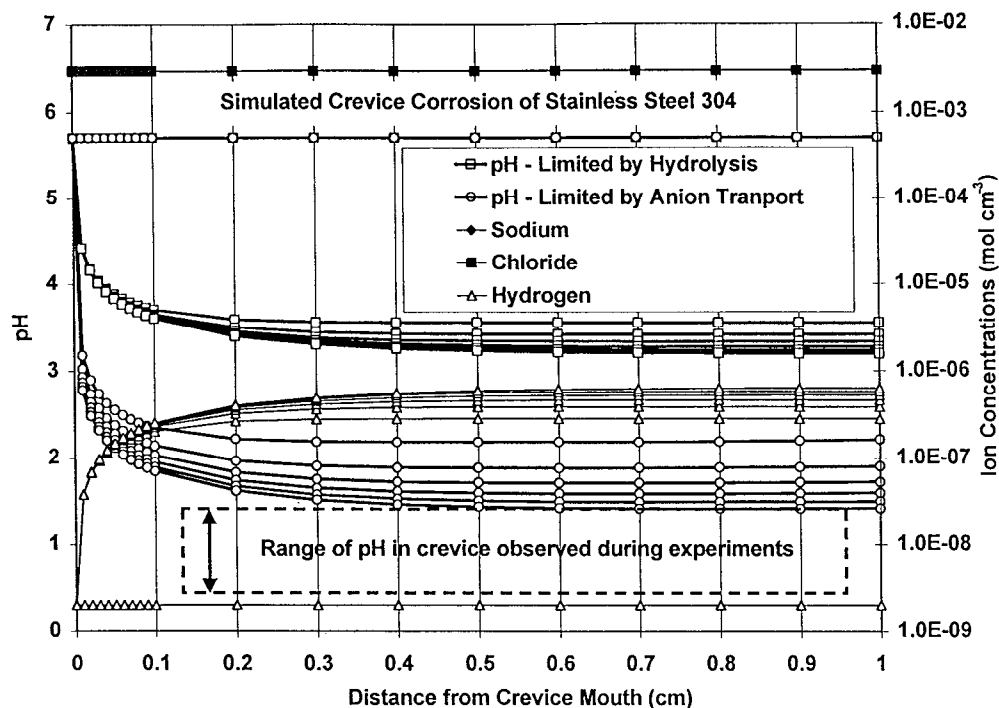


Figure 1. Simulated crevice corrosion of Type 304 stainless steel in saturated NaCl at 25°C with applied potential of 0.4 V vs. SCE. Predicted pH profiles at 600-second increments with lowest predicted levels at 3600 seconds.

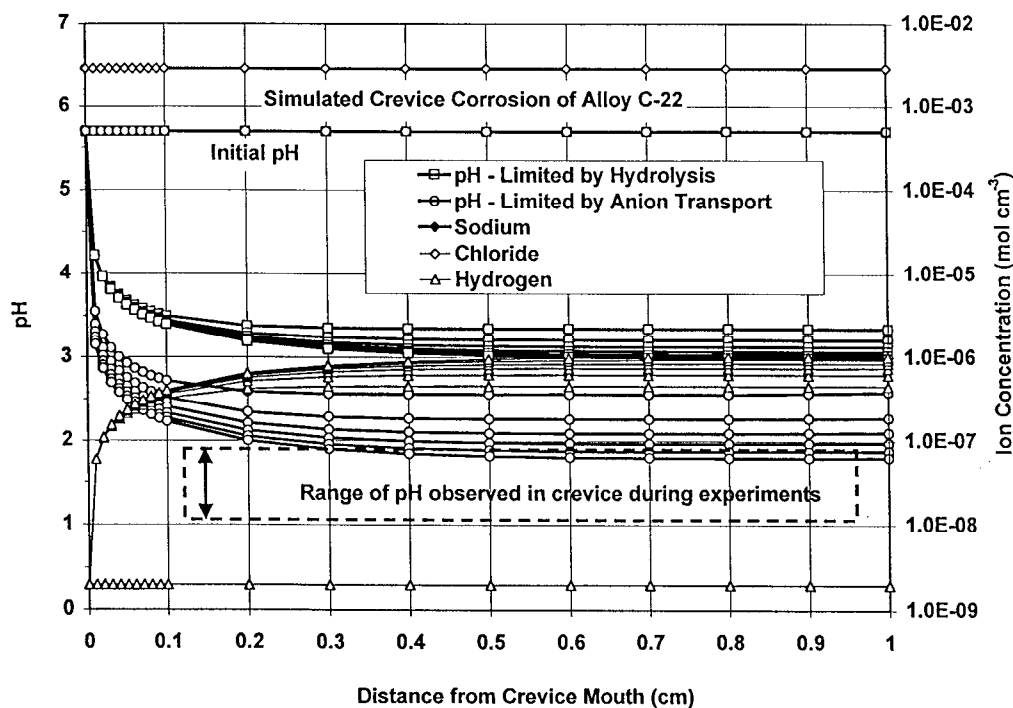


Figure 2. Simulated crevice corrosion of Alloy 22 in saturated NaCl at 25°C with applied potential of 0.8 V vs. SCE. Predicted pH profiles at 600-second increments with lowest predicted levels at 3600 seconds.



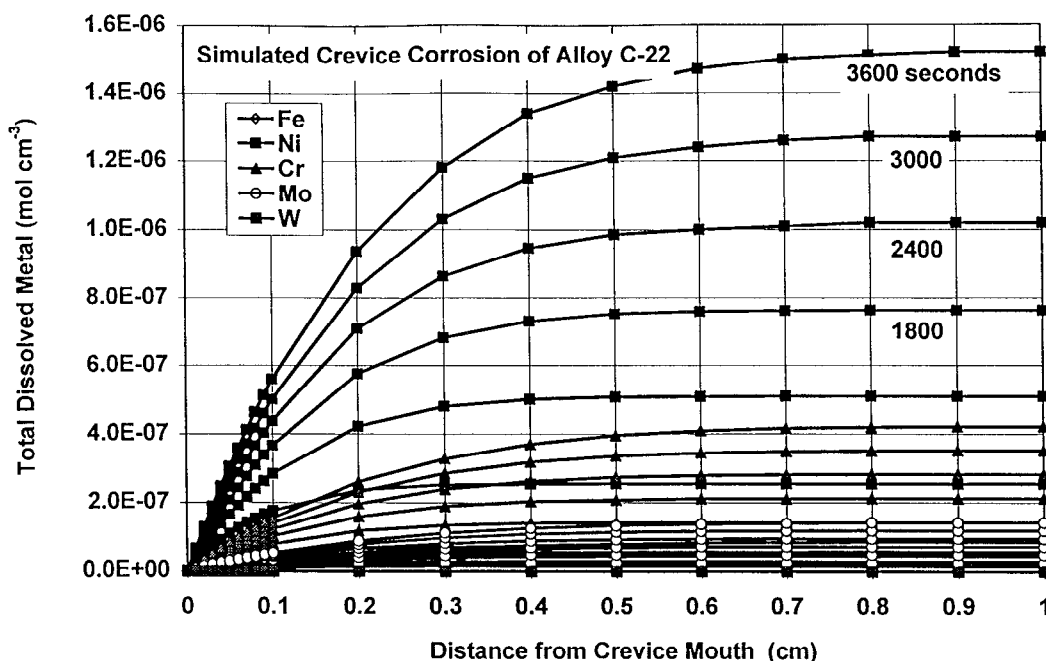


Figure 3. Simulated crevice corrosion of Alloy 22 in saturated NaCl at 25°C with applied potential of 0.8 V vs. SCE. Predicted dissolved metal profiles at 600 second intervals with the highest values at 3600 seconds. Corresponds to Figure 2.

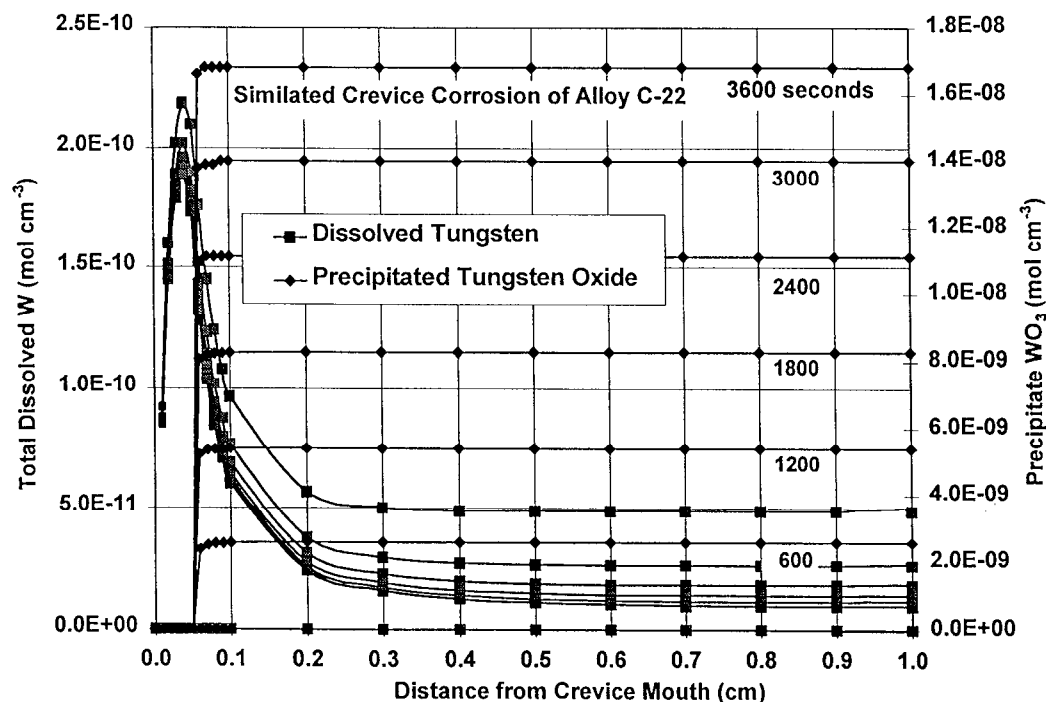


Figure 4. Simulated crevice corrosion of Alloy 22 in saturated NaCl at 25°C with applied potential of 0.8 V vs. SCE. Predicted profiles for dissolved W and precipitated  $\text{WO}_3$  at 600-second intervals with the highest values at 3600 seconds. Corresponds to Figure 2.

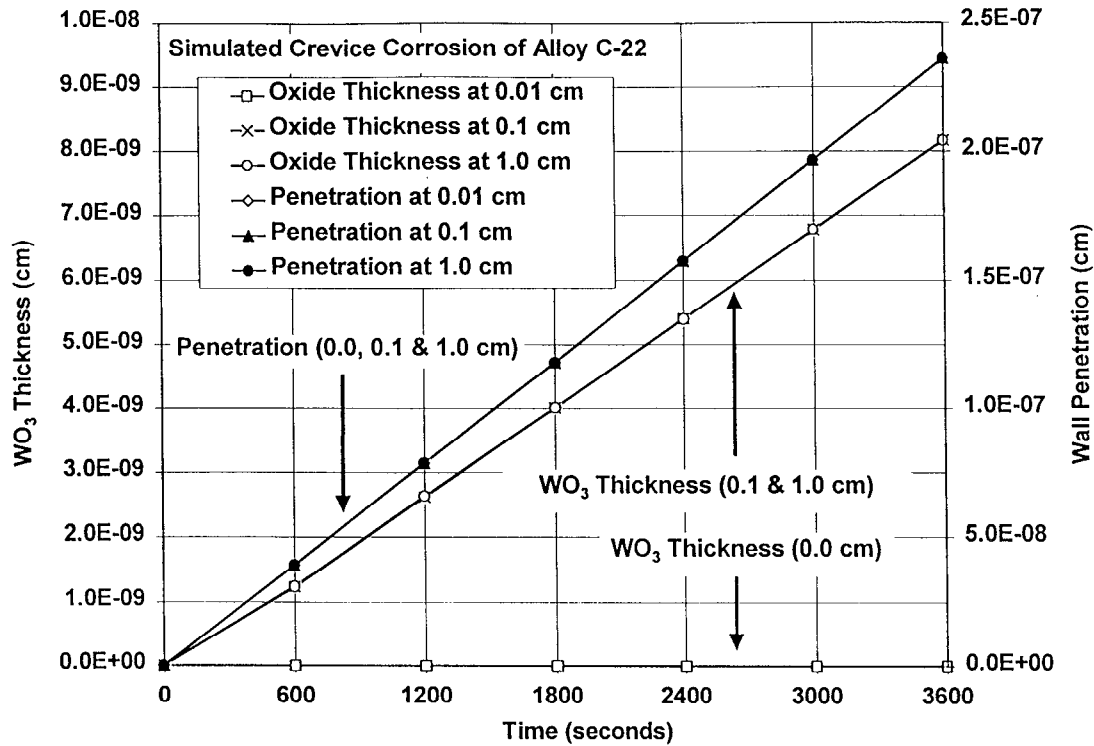


Figure 5. Simulated crevice corrosion of Alloy 22 in saturated NaCl at 25°C with applied potential of 0.8 V vs. SCE. Predicted wall penetration and WO<sub>3</sub> thickness at 0.01, 0.1 and 1.0 cm from the crevice mouth. Corresponds to Figure 2.

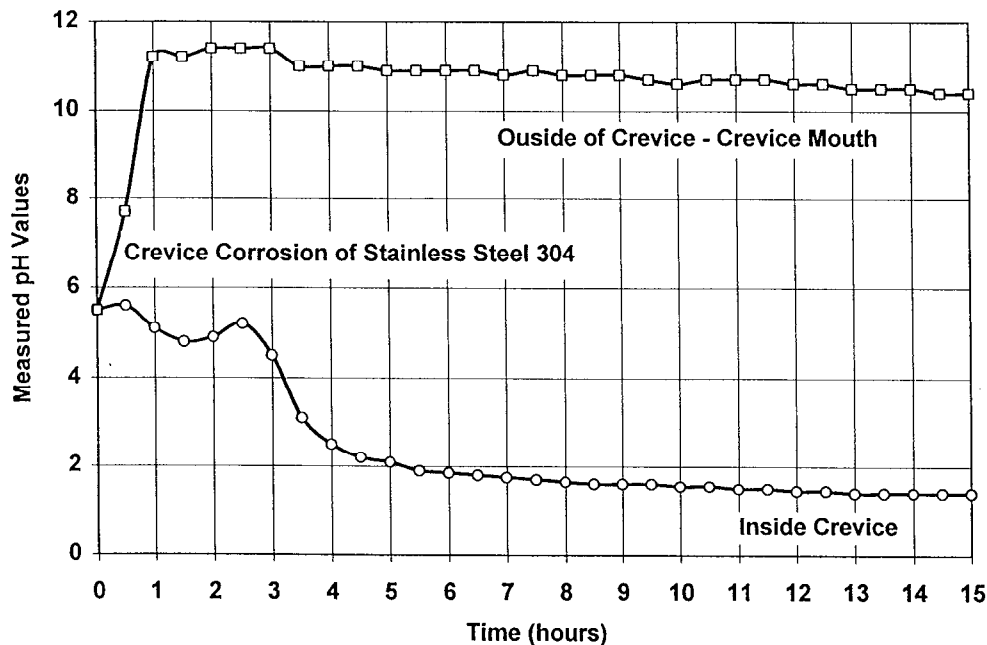
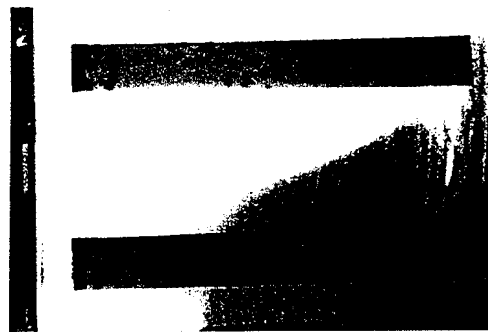


Figure 6. Measured pH during crevice corrosion of 304 stainless steel in saturated KCl at 25°C with applied potential of 0.8 V vs. SCE. Measured values confirmed with indicator.

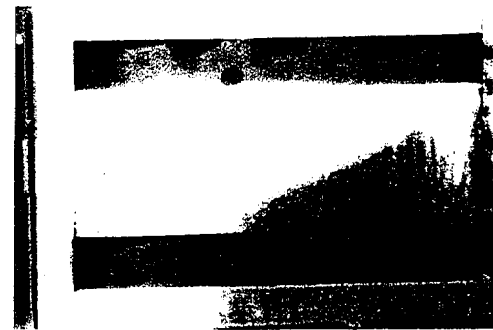
# Crevice Corrosion of Stainless Steel 304



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9:23:24 (+0.800 V)



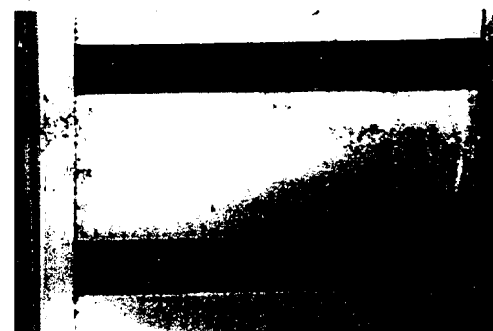
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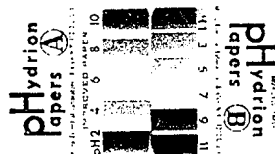
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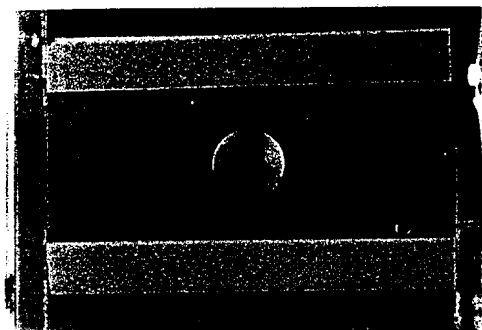
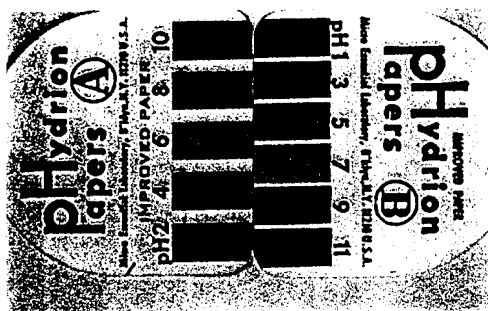
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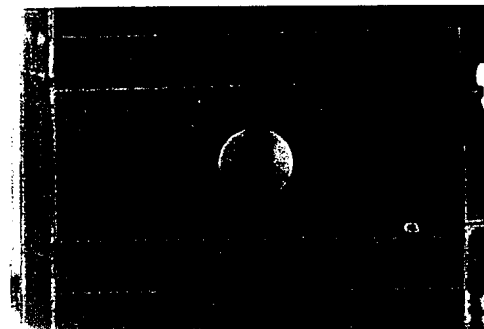
10:07:00 (+0.800 V)



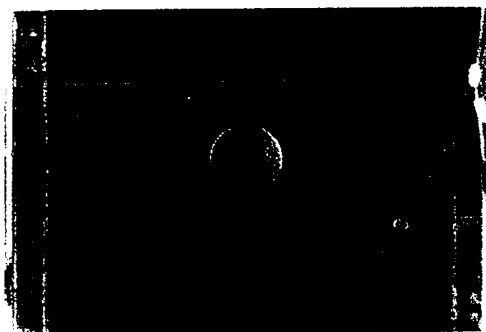
## Crevice Corrosion of Alloy C-22



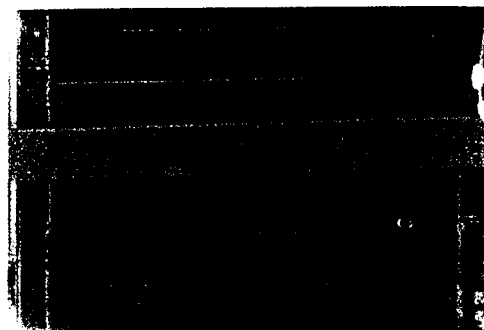
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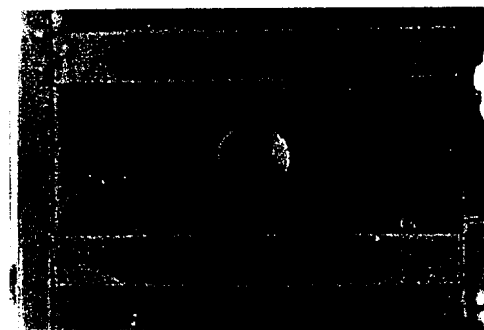
10:40:00 (+0.800 V)



11:00:00 (+0.800 V)



11:15:02 (+0.800 V)



11:43:33 (+1.200 V)